

Appl. No. 10/025,647
Amdt. Dated: January 22, 2004
Reply to Office Action of 10/08/2003
Attorney Docket No. MSU 4.1-568

This listing of claims will replace all prior versions and listings of claims in the application:

LISTING OF CLAIMS

-1- (Currently Amended)

A porous structured aluminosilicate composition which comprises:

a framework of linked tetrahedral SiO_4 and AlO_4 units assembled from zeolite fragments, the framework defining pores and having a Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and wherein the composition retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours.

-2- (Currently Amended)

A porous structured aluminosilicate composition which comprises:

a framework of linked SiO_4 and AlO_4 units assembled from zeolite fragments, the framework defining pores and having a Si to Al molar ratio of about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak between 2 and 100 nm, and wherein the composition retains at least 75% of an initial framework pore volume after exposure to 20 volume percent steam at 600°C for four hours.

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-3- (Currently Amended)

The composition of Claims 1 or 2 assembled from preformed zeolite seeds and or zeolite fragments.

-4- (Original)

The composition of Claims 1 or 2 having a BET surface area of between about 200 and 1400 m^2 per gram, an average pore size between about 1 and 100 nm and a pore volume of between about 0.1 and 3.5 cm^3 per gram.

-5- (Original)

The composition of Claim 3 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

-6- (Currently Amended)

A porous structured aluminosilicate composition
which comprises:

5 a framework of linked tetrahedral SiO_4 and AlO_4
units, the framework defining pores having an organic
surfactant in the pores and having a Si to Al molar ratio
of between 1000 to 1 and 1 to 1 and having at least one
X-ray diffraction peak corresponding to a basal spacing
between about 2 and 100 nm and wherein the composition is
derived from a porogen and preformed ~~zeolite seeds~~ or
10 zeolite fragments.

-7- (Original)

The composition of Claim 6 wherein the porogen
is an organic surfactant is selected from the group
consisting of an organic onium ion surfactant and a non-
ionic surfactant.

-8- (Original)

The composition of Claim 7 wherein the
surfactant is a non-ionic surfactant selected from the
group consisting of a non-ionic polyethylene oxide
surfactant and a non-ionic amine surfactant.

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-9- (Original)

The composition of Claim 6 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

-10- (Original)

The composition of Claim 1, 2 or 3 containing between about 0.1 and 50% by weight carbon in the framework pores.

-11- (Original)

The composition of Claims 1 and 2 with an infrared absorption band between 500 and 600cm⁻¹.

-12- (Original)

The composition of Claim 6 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkyl amine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

-13- (Withdrawn)

10 A process for forming a porous aluminosilicate composition which comprises:

15 (a) providing zeolite seeds or zeolite fragments in a form selected from the group consisting of an aqueous solution, gel, suspension wetted powder and mixtures thereof;

(b) mixing in a mixture the zeolite seeds or zeolite fragments in an aqueous medium with an organic porogen;

20 (c) aging the mixture of step (b) at a temperature between 25° and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c).

-14- (Withdrawn)

The process of Claim 13 wherein the porogen is a surfactant.

-15- (Withdrawn)

The process of Claim 14 wherein the organic surfactant is selected from the group consisting of onium ion surfactants and non-ionic surfactants.

-16- (Withdrawn)

The process of Claim 13 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkylamine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

-17- (Withdrawn)

The process of Claims 13 or 14 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

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-18- (Withdrawn)

The process of Claims 13 or 14 wherein in addition the composition is calcined.

-19- (Withdrawn)

The process of Claims 13 or 14 wherein in addition the composition is calcined at above about 400°C.

-20- (Currently Amended)

A structured aluminosilicate porous composition
which comprises:

a framework of linked tetrahedral SiO_4 and AlO_4
units assembled from zeolite fragments, the framework
5 defining mesopores, having a porogen in the pores of the
composition, having a an Si to Al molar ratio of between
about 1000 to 1 and 1 to 1, and having at least one X-ray
diffraction peak corresponding to a basal spacing between
about 2.0 and 100 nm, and which when calcined retains at
10 least 50% of an initial framework pore volume after
exposure to 20 volume % steam at 800°C for two hours.

-21- (Original)

The composition of Claim 20 wherein the porogen is a surfactant is selected from the group consisting of:

(a) an ammonium or phosphonium ion of the formula $R_1R_2R_3R_4Q^+$, wherein Q is nitrogen or phosphorous, and wherein at least one of the R moieties is selected from the group consisting of aryl, alkyl of between about 5 6 to 36 carbon atoms and combinations thereof, remaining of the R moieties are selected from the group consisting of hydrogen, alkyl of from 1 to 5 carbon atoms and combinations thereof, and

(b) a non-ionic block surfactant containing polyethylene oxide units in a hydrophilic block and polypropylene oxide, polybutylene oxide, alkyl, or aryl units in a hydrophobic block, and nonionic amine 10 surfactants containing 6 to 36 carbon atoms.

-22- (Original)

The composition of Claim 20 wherein the porogen is a surfactant and a co-surfactant and the co-surfactant is selected from the group alkyl amine, alkyl alcohol, aromatic hydrocarbon and mixtures thereof, wherein the 5 number of carbon atoms in the co-surfactant is between 2 and 36.

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-23- (Original)

The composition of any one of Claims 1, 2, 6 or 20 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole or cellular foam.

-24- (Original)

The composition of Claims 6 or 20 wherein the porogen is removed by calcination, by ion exchange, or by a combination of ion exchange and calcination.

-25- (Currently Amended)

A porous aluminosilicate composition which comprises: a framework of tetrahedral linked SiO_4 and AlO_4 units assembled from zeolite fragments, the framework defining mesopores having an Si to Al molar ratio of 5 between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 10 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours.

-26- (Original)

The composition of Claim 25 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole, or cellular foam.

-27- (Currently Amended)

A hybrid porous aluminosilicate - carbon composition which comprises: a framework of linked tetrahedral SiO_4 and AlO_4 units assembled from zeolite fragments, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 100 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours.

-28- (Original)

The composition of Claim 27 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole, or cellular foam.

-29- (Original)

A composition prepared by treating the composition of Claim 20 before calcining with an ammonium salt solution at a temperature between about 0° and 200°C for a period of up to 24 hours and repeating the 5 treatment up to ten times to introduce ammonium ions into the composition, collecting and drying the resulting composition, and then calcining the resulting composition at a temperature between about 400 and 900°C to remove the organic porogen and to convert a fraction of the 10 surfactant or other organic porogen to carbon embedded in the mesopores.

-30- (Withdrawn)

A process for forming a porous aluminosilicate composition which comprises:

(a) reacting a sodium silicate solution at basic pH with a sodium aluminate solution at an aluminum to silicon ratio between about 1000 to 1 and 1 to 1 and aging the mixture at 25 to 200°C for periods of up to 48 hours to form zeolite seeds;

(b) mixing the resultant mixture with an organic porogen;

(c) reducing a pH of the mixture obtained from (b) with a protonic acid to obtain a mixture with an OH⁻ / (Si+Al) ratio in the range of 0.10 to 10;

(d) aging the mixture from step (c) at a temperature between 20 and 200°C to obtain a precipitate of the composition; and

(e) separating the composition from mixture of step (d).

-31- (Withdrawn)

The process of Claim 30 wherein the sodium silicate is prepared by reacting sodium hydroxide with a silicon source selected from the group consisting of a colloidal silica, a fumed silica, a silica gel, a silicon alkoxide and mixtures thereof.

-32- (Withdrawn)

The process of Claim 30 wherein the sodium aluminate is prepared by reacting sodium hydroxide with an aluminum source selected from the group consisting of a soluble aluminum salt, a cationic aluminum oligomers, 5 an aluminum hydroxide, an aluminum oxide, an aluminum alkoxide and mixtures thereof.

-33- (Withdrawn)

The process of Claim 30 wherein the organic porogen is a surfactant selected from the group consisting of:

(a) a alkyl quaternary ammonium surfactant with a hydrophobic segment which contains between 8 to 36 carbon atoms,

(b) a non-ionic surfactant containing a polyethylene oxide block as a hydrophilic segment, and

(c) a non-ionic amine surfactant.

-34- (Withdrawn)

The process of Claim 30 wherein the composition has a ^{27}Al -NMR resonance line exhibiting a chemical shift in the range of 57 to 65 ppm relative to an external reference of 1.0 M aluminum nitrate.

-35- (Withdrawn)

A process for forming a porous aluminosilicate composition which comprises:

(a) providing zeolite seeds or zeolite fragments in a form selected from the group consisting of an aqueous solution, gel, suspension, wet powder, or combination thereof;

(b) reacting the zeolite seeds in the aqueous medium with an organic porogen wherein the solution has an $\text{OH}^-/(\text{Si}+\text{Al})$ ratio in the range of 0.10 to 10;

(c) aging the mixture from step (b) at a temperature between 20 and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c).

-36- (Withdrawn)

A catalyst useful for a fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

5 (a) a porous aluminosilicate composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

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15 (b) a binder for the aluminosilicate composition.

-37- (Withdrawn)

A catalyst useful for fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

(a) a porous aluminosilicate - carbon composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 100 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, wherein the carbon content is between 0.01 and 50% by weight, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) a binder for the aluminosilicate-carbon composition.

-38- (Withdrawn)

A process for catalytic reaction of an organic molecule into lower molecular weight components, which comprises:

(a) providing in a reactor a catalytic cracking catalyst which comprises: a porous aluminosilicate composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram; and a binder for the aluminosilicate composition, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule.

-39- (Withdrawn)

A process for reaction of an organic molecule into lower molecular weight components, which comprises:

(a) providing in a reactor a catalytic cracking catalyst which comprises: a porous aluminosilicate - carbon composition which comprises: a framework of tetrahedral linked SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 100 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram; and a binder for the aluminosilicate-carbon composition, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule into lower molecular weight components.

-40- (Withdrawn)

A catalyst useful for a fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

5 (a) a porous structured aluminosilicate composition which comprises:

10 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining pores and having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and wherein the composition retains at least 50% of the initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) a binder for the aluminosilicate composition.

-41- (Withdrawn)

A process for reaction of an organic molecule into lower molecular weight components which comprises:

(a) providing a porous structured aluminosilicate composition which comprises:

5 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining pores and having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 1 and 100 nm, and
10 wherein the composition retains 50% of the initial framework pore volume upon exposure to 20 volume percent steam at 800°C for two hours; and

15 (b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule to produce the lower molecular weight components.

-42- (Withdrawn)

In a catalyzed organic reaction process, the improvement which comprises:

conducting the reaction with a catalyst which is selected from the group consisting of a porous structured aluminosilicate, gallosilicate, titanosilicate and mixtures thereof which catalyst comprises: a framework of linked tetrahedral SiO_4 and AlO_4 , GaO_4 or TiO_4 units, the framework defining pores and having an Si to combined Ga, Ti and Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2 and 100 nm, and wherein the composition retains at least 50% of initial framework pore volume after exposure to 20 volume % steam at 600°C for four hours.

-43- (Currently Amended)

A porous structured silicate composition which comprises:

a framework of linked tetrahedral SiO_4 and units selected from the group consisting of AlO_4 units, GaO_4 units, TiO_4 units and mixed units assembled from zeolite fragments, the framework defining pores and having an Si to combined Ga, Ti and Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 1 and 100 nm, and wherein the composition retains at least 50% of the initial framework pore volume after exposure to 20 volume percent steam at 600°C for four hours.

-44- (Original)

The composition of Claim 43 assembled from preformed nanoclustered seed precursors.

-45- (Original)

The composition of Claims 43 or 44 having an X-ray diffraction peak corresponding to a basal spacing between about 2 and 100 nm, a BET surface area of between about 200 and 1400 m^2 per gram, an average pore size between about 1 and 100 nm and a pore volume of between about 0.1 and 3.5 cm^3 per gram.

-46- (Original)

The composition of Claim 44 wherein the seed precursors are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

-47- (Original)

The composition of Claims 1 and 2 with a ^{27}Al NMR chemical shift between about 57 and 65 ppm relative to an external reference of 1.0 M aluminum nitrate.

-48- (Original)

The composition of Claim 1 which contains zeolite crystals.

-49- (Original)

The composition of Claim 2 which contains zeolite crystals.

-50- (Original)

The composition of Claim 6 which contains zeolite crystals.

-51- (Original)

The composition of claim 6 wherein the zeolite fragments are derived from zeolite crystals by digesting with a base.

-52- (Original)

The composition of Claim 6 wherein the zeolite fragments are derived from a naturally occurring crystalline zeolite.

-53- (Withdrawn)

The process of Claim 13 wherein seeds are aged to form zeolite crystals in step (a) prior to addition of the organic porogen.

-54- (Withdrawn)

The process of Claim 13 wherein the zeolite fragments in step (a) are produced by digesting zeolite crystals with a base.

-55- (Withdrawn)

The process of Claim 13 wherein the zeolite fragments are derived from naturally occurring zeolite crystals.

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-56- (Original)

The composition of Claim 27 which contains zeolite crystals.

-57- (Withdrawn)

The catalyst of Claim 36 which contains zeolite crystals.

-58- (Withdrawn)

The catalyst of Claim 37 which contains zeolite crystals.

-59- (Withdrawn)

The process of Claim 38 wherein the catalyst contains zeolite seeds.

-60- (Withdrawn)

The process of Claim 39 wherein the catalyst contains zeolite seeds.

-61- (Withdrawn)

The catalyst of Claim 40 which contains zeolite crystals.

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-62- (Withdrawn)

The process of Claim 41 wherein the catalyst contains zeolite seeds.

-63- (Withdrawn)

The reaction of Claim 42 where the catalyst contains zeolite seeds or zeolite fragments.

-64- (Currently Amended)

The composition of Claim 43 wherein the catalyst contains zeolite seeds and or zeolite fragments.

-65- (Withdrawn)

A process for forming a porous aluminosilicate composition which comprises:

(a) providing zeolite fragments prepared by disrupting the structure of a crystalline aluminosilicate zeolite in a form selected from the group consisting of an aqueous solution, gel, suspension, wetted powder, and mixtures thereof;

(b) mixing in a mixture the zeolite fragments in an aqueous medium with an organic porogen;

(c) aging the mixture of step (b) at a temperature between 25° and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c)..

-66- (Withdrawn)

The process of Claim 65 wherein the fragments are formed by disrupting the structure of a synthetic or naturally occurring zeolite.

-67- (Withdrawn)

The process of Claim 65 or 66 wherein the organic porogen is an organic surfactant selected from the group consisting of onium ion surfactants and non-ionic surfactants.

-68- (Withdrawn)

The process of Claim 65 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkylamine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

-69- (Withdrawn)

The process of Claim 65 wherein the zeolite fragments are formed by disrupting the structure of a zeolite through treatment with a base or by subjecting the zeolite to ultrasound, grinding, milling or a combination thereof.

-70- (Withdrawn)

The process of Claim 65 or 66 wherein in addition the composition is calcined.

-71- (Withdrawn)

The process of Claim 65 or 66 wherein in addition the composition is calcined at above about 400°C.

-72- (Original)

The process of Claim 20 wherein the porogen is a non-surfactant.

-73- (Original)

The process of Claim 20 wherein the porogen is triethanolamine.

-74- (Original)

A product prepared by the process of Claim 65.

-75- (Original)

The composition of Claim 1 having at least one x-ray diffraction peak corresponding to a basal spacing of about 2 and 100 nm.

-76- (Original)

The composition of Claim 1 having no x-ray diffraction peaks.

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-77- (Withdrawn)

The process of Claim 13 wherein the zeolite fragment is formed from a crystalline zeolite selected from a group consisting of zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZMS-11, zeolite Beta, and zeolite MCM-22.

-78- (Withdrawn)

The process of Claim 13 wherein the zeolite fragment is formed from MCM-22(P), the precursor of zeolite MCM-22.

-79- (Original)

A carbon composition obtained from the composition of any one of Claims 27, 28 or 29, wherein the aluminosilicate component is removed by dissolving in aqueous base or hydrofluoric acid.

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-80- (Original)

The composition of Claim 6 wherein the porogen is selected from the group consisting of an amine, ethoxylated amine or alkoxylated amine.

-81- (Withdrawn)

The process of Claim 13 wherein the zeolite fragment is formed from a crystalline zeolite or a crystalline zeolite precursor.

-82- (Currently Amended)

The composition of Claim 6 wherein the zeolite seeds and or fragments are derived from a crystalline aluminosilicate.

-83- (Original)

The composition of Claim 82 wherein the crystalline aluminosilicate is a clay.